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COMBUSTION RESEARCH FACILITY
SANDIA NATIONAL LABORATORIES / CALIFORNIA

Mixture preparation in a hydrogen-fueled engine

The hydrogen-fueled internal combustion engine (H_2ICE) is a promising power plant that bridges to future propulsion technologies in the "hydrogen economy". Direct injection (DI) of the hydrogen gas into the cylinder is an essential part of all advanced strategies for H_2ICEs. With hydrogen DI, it is possible to increase the power density, mitigate problems of backflash and pre-ignition, and improve on the trade-off in NO_x emissions versus fuel efficiency. However, detailed knowledge about the impact of DI on the charge preparation during the compression stroke, which controls ensuing combustion in the power stroke, is essential.

At the Hydrogen Engine Lab, Sebastian Kaiser and Chris White, now Assistant Professor, Mechanical Engineering Department, University of New Hampshire, are studying the influence of the injection event on in-cylinder flow and hydrogen-air mixing by applying laser-based measurements to an optically accessible DI-H_2ICE. Providing a science base for the optimization of hydrogen engines, these studies are complemented by the work of collaborating groups at Argonne National Lab and Ford R&D, where all-metal engines are used for thermodynamic analysis of extensive parameter sweeps.

New energetic polymers show promise as binder replacements for development of next generation insensitive munitions

Future munitions development calls for increased performance of the explosive or propellant formulations used in the munitions, while also satisfying strict new vulnerability assessments. Design criteria for these new munitions call for improved mechanical response, extended service life, enhanced safety during handling, storage, and transport, and a reduced environmental impact from manufacture through disposal. As current munition designs are phased-out over the next few decades, the timing for the introduction of new replacement materials that will meet these stricter performance and safety requirements is critical.

The U.S. Naval Surface Warfare Center, Indian Head Division (NSWC-IH) has recently concluded a three-year study to investigate the combustion chemistry of new energetic ingredients and polymeric binders with potential for increased energy storage
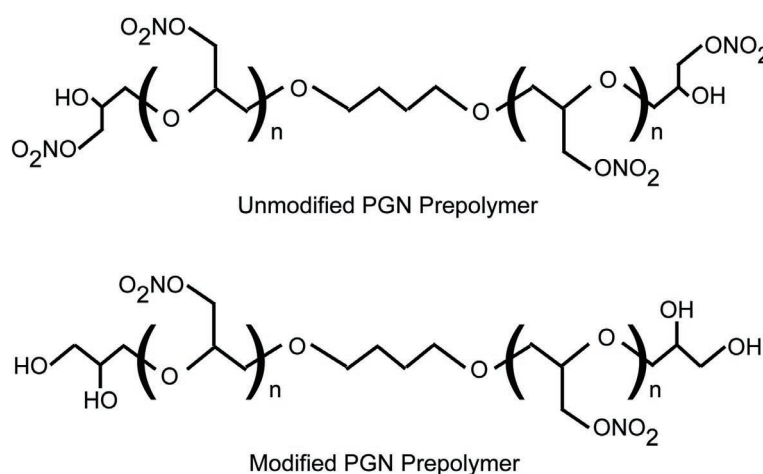
Figure 1. Structural representation of the polyglycidyl nitrate (PGN) uncured prepolymers. Upper illustration shows the unmodified prepolymer; the lower illustration shows the OH end-capped (modified) prepolymer.

Extensive programs have been developed worldwide over the last decade for the development and introduction of insensitive munitions (IM), ordnance that meet performance goals while showing reduced adverse response to unplanned hazardous stimuli. Several approaches are available to meet IM requirements, including overall weapon design, mitigation devices, and packaging, although the most obvious and broadly studied approach is development of intrinsically less sensitive explosive and propellant formulations.

(performance) and decreased sensitivity to hazardous stimuli (IM compliance). Various new energetic binder materials were investigated in an attempt to increase the energy content of propellant formulations. The nitrate-ester prepolymer PGN (polyglycidyl nitrate – Figure 1) has high oxygen balance and energy density, making it the most energetic nitrate ester polymer being considered for use in new munitions. However, when PGN is cured using aliphatic diisocyanate-derivative curing agents, it exhibits poor aging characteristics. PGN may be a suitable

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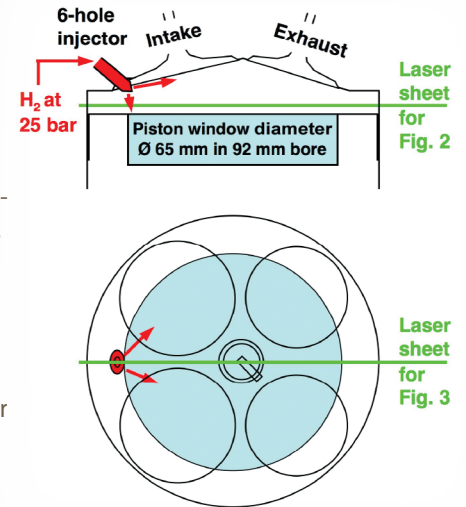# Mixture preparation (continued)

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As a starting point, injection from the side using a 6-hole injector pressurized to 25 bar was investigated. The general geometry of the experiment is shown in Figure 1. At 1200 rpm and an overall equivalence ratio of $\phi = 0.55$, images are taken at 32° before top dead center (BTDC) of the compression stroke.

Figure 2 shows results from two different injection timings: Early injection (immediately after intake valve close, 112° to 62° BTDC) and late injection (90° to 40° BTDC). Planar laser-induced fluorescence of acetone, seeded into the hydrogen fuel, was used to quantitatively measure the local equivalence ratio (ϕ). For early injection the fuel distribution is relatively homogenous, while for late injection we find that high fuel concentrations ($\phi > 1$) close to the injector are sharply separated from low concentrations ($\phi < 1$) elsewhere. Particle image velocimetry was then applied to image the in-cylinder flow (velocity vector $\vec{v}$) for the same conditions. We find that the injection event strongly influences the flow. Early injection yields randomly distributed turbulence. In contrast, the sample single-shot vector field for late injection shows a line of shear-induced eddies separating very turbulent flow near the injector from the smoother flow field away from the injector. In the mean, the main features of fuel distribution and velocity field correspond very well. In particular, we can see that for late injection the fuel-rich region corresponds to flow away from the injector, meeting fuel-lean fluid flowing towards the injector in a broad counter flow. This counter-flow pattern is thought to keep the fuel close to the issuing nozzles and inhibit mixing, hence the strong inhomogeneity in the equivalence-ratio field.

To investigate the injection-induced flow in more detail, we also made velocity measurements in the central vertical plane (see geometry sketch in Figure 1). Results for late injection are shown in Figure 3. Based on the velocity measurements in the two planes, we conjecture that the flow field for this injection timing can be approximately summarized as shown in the schematic, as follows: flow from those jets that are roughly oriented along the pent-roof is re-directed by the walls and the cylinder top, while diluting due to entrainment of air. This flow meets the fuel-rich flow from those orifices that point downwards onto the piston top. This situation creates the upward-sweeping counter flow that we see in the mean vector field of Figure 3.

Figure 1. *Sketch of cylinder and imaging geometry for horizontal and vertical imaging planes (Figs. 2 and 3, respectively).*
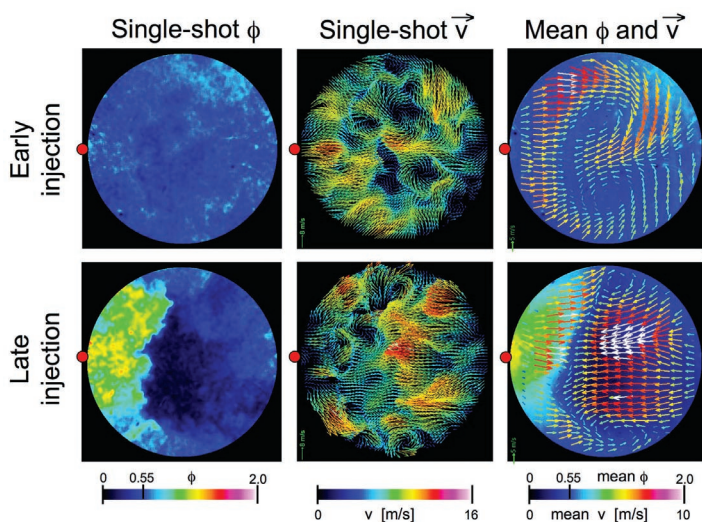
Figure 2. *Fuel distribution and velocity at 32° BTDC for two different hydrogen injection timings.*

We conclude that, when side-mounted, the 6-hole injector is not suitable for use with late injection timings because fuel concentrates near the cylinder wall, which leads to high heat loss during combustion in the fired engine. A similar injector geometry was investigated at Argonne National Lab, and it was indeed found that retarding the start of injection past 100° BTDC resulted in a marked drop-off in thermal efficiency. With the experience gained with the two diagnostics used for the study summarized here, we are now in the process of investigating the effects of different injector locations and injector tip geometries on the mixture formation.
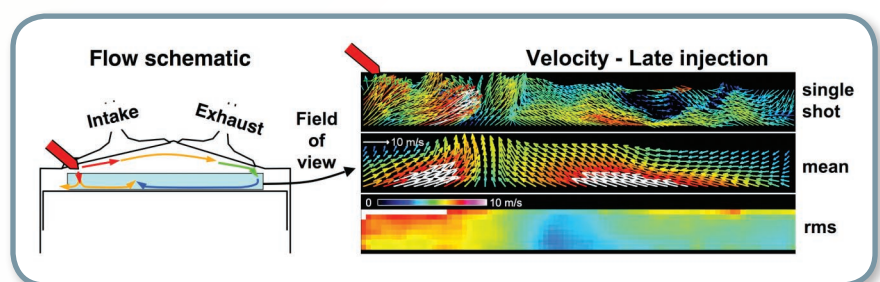
Figure 3. *Schematic of the injection-induced flow (left) and the velocity field with late injection (right).*

Advanced Engine Combustion and University HCCI working group meetings held

The Advanced Engine Combustion (AEC) and the University Homogeneous Charge Compression Ignition (HCCI) Engine Combustion working group meetings, organized by Sandia National Laboratories, were held in March at Sandia's Combustion Research Facility in Livermore California. A highlight of the meeting was presentations by six industry partners on their views on research needs for the future related to engines and fuels. The latest results from the DOE Office of Vehicle Technologies supported research on advanced, low-temperature combustion strategies for high-efficiency, clean engines and future fuels for these engines were also presented and discussed. More than 100 representatives from industry, national labs and universities attended the meetings. Attendees included representatives from GM, Ford, Chrysler, Cummins, Detroit Diesel, Caterpillar, John Deere, General Electric, Chevron, ExxonMobil, ConocoPhillips, BP, SNL, LLNL, LANL, ORNL, and ANL, all members of the AEC Memorandum of Understanding (MOU). University attendees from Michigan, Wisconsin, MIT, Illinois, and Stanford joined the group for the University HCCI working group portion of the meeting.

John Dec of the CRF with members of the AEC and HCCI working group (above).

*Attendess of the working group meetings*

CRF visitors

Professor John Abraham of Purdue University is currently visiting the CRF on a one-year faculty sabbatical. With an extensive background in internal combustion engines and CFD, Professor Abraham is collaborating with CRF engine combustion researchers on topics such as HCCI, sprays, and flame lift-off stabilization.

Glen Martin recently completed his post-doctoral research with Sandia Principal Investigator (PI) Chuck Mueller in the Advanced Fuels Laboratory, where he helped develop a fundamental understanding of the mechanisms governing emissions and efficiency in early-direct-injection, low-temperature-combustion strategies employing diesel and other fuels. Glen is now an employee at the Caterpillar Technical Center in Mossville, Illinois, where he is developing new experimental hardware and advanced laser/imaging diagnostic capabilities for the study of high-pressure spray flames.
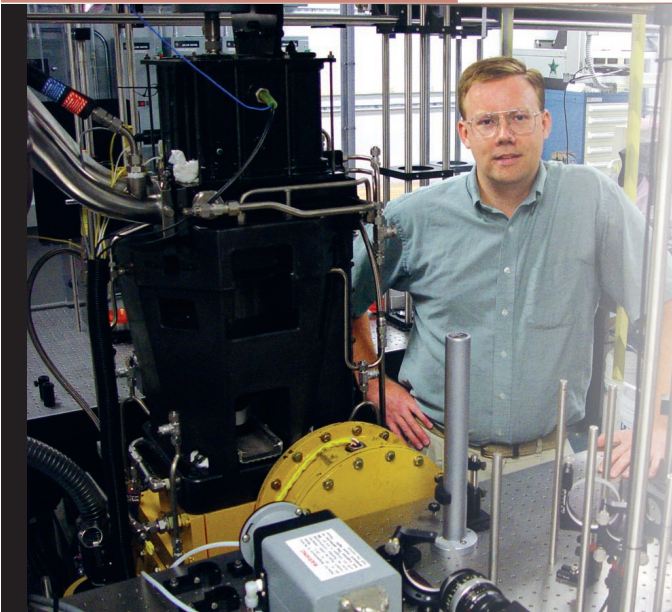
In March, Michael Oevermann of the Technical University of Berlin and Heiko Schmidt of the Free University of Berlin visited CRF researcher Alan Kerstein to pursue collaborative work on turbulent flow modeling. Together they are performing computer simulations of engine processes and cloud dynamics.

Alan Kerstein

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candidate for new munitions, if its properties remain stable after the pre-polymer is cured. To improve long-term stability, both the Defence Evaluation and Research Agency (DERA) and Imperial Chemical Industries (ICI) have used ethylene oxide to end cap the PGN prepolymer with a polyol.

Figure 2. *Ion signals, formed in the STMBMS, representing the products formed during the decomposition of unmodified and modified PGN. Data shown in panels A, B, C and D represent the products formed in each of four reaction pathways.*

In collaborations with Chad Stoltz (NSWC) and Suhithi Peiris (DTRA), Sandia researchers Sean Maharrey and Richard Behrens have used the Simultaneous Thermogravimetric Modulated Beam Mass Spectrometer (STMBMS) and Fourier-Transform Ion-Cyclotron Resonance Mass Spectrometer (FTICR/MS) located at the Combustion Research Facility to investigate the low temperature thermal decomposition processes for both the unmodified and OH end-capped (modified) PGN prepolymers. STMBMS and FTICR/MS thermal decomposition experiments on the unmodified and modified PGN prepolymers provide insight into the dominant reaction mechanisms controlling the decomposition behavior and the effect chemical chain modification has on this process. An understanding of these reaction processes can be used to assess both the compatibility of new ingredients with the PGN binder, and any long-term aging issues corresponding to the use of PGN.
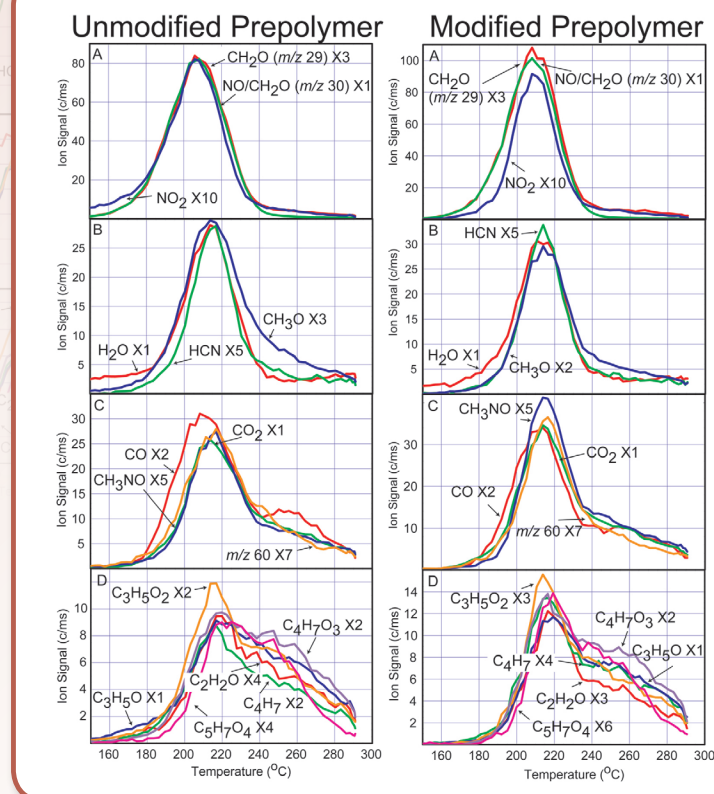
Careful examination of the ion signals formed in the STMBMS and representing the products formed during the decomposition of the unmodified and modified PGN prepolymers, can be divided into four temporally correlated groups as shown in Figure 2. The products in each of these groups can be associated with a sequence of steps in the reaction process that controls the thermal decomposition of the PGN prepolymers as summarized in the reaction scheme shown in Figure 3.

Chemical modification of the terminal end of the prepolymer by replacing the terminal nitrate ester ($O-NO_2$) by OH has no effect on the overall decomposition process. The principal difference observed between the unmodified and modified PGN decomposition is the early evolution of NO_2 with the unmodified PGN from the terminal nitrate ester end-group. The early evolution of NO_2 does not have an observed effect on the rest of the decomposition process. The similar decomposition process for the unmodified and end-modified PGN prepolymers is consistent with the dominant reactions being elimination of the CH_2-O-NO_2 nitrate ester functional group and subsequent reactions of the gas products with the remaining backbone.

Reaction pathway P1 (data in panel A in Figure 2) corresponds to the elimination and decomposition of the CH_2-O-NO_2 functional moiety to form principally CH_2O and NO_2, which leaves behind a highly reactive backbone from the nitrate ester elimination. Note that the products formed

New energetic polymers (continued)

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in this pathway start to evolve prior to the evolution of products in the other pathways. This fact suggests that elimination of the CH_2-O-NO_2 functional moiety is the first step in the decomposition process. Careful comparison of the temporal behavior of the signals from CH_2O, NO and NO_2 for the unmodified and modified prepolymers shows that the products formed from the unmodified prepolymers start to evolve at a somewhat lower temperature (160°C) compared to the OH-modified prepolymers (~180°C). This temperature difference may be associated with the decomposition of the nitrate ester end groups in the unmodified PGN prepolymers.

Reaction pathway P2 represents the global reaction of CH_2O with NO_2 to form H_2O, CO and NO products. Reaction pathways P3 and P4 (data in panels B and C in Figure 2) represent two reactions that can control the unzipping of the reactive backbone structure to form either H_2O and HCN or CO, CO_2 and CH_3NO via an interaction with NO/NO_2. Reaction pathways P3 and P4 unzip the reactive backbone until nearing the butyl moiety. The butyl moiety apparently reacts to form a non-volatile residue (pathway P5), which subsequently decomposes slowly to form a distribution of $C_xH_yO_z$ species, pathway P6 (data shown in panel D of Figure 2).

The gas-phase products evolved from the condensed-phase thermal decomposition process form the reactant "pool"
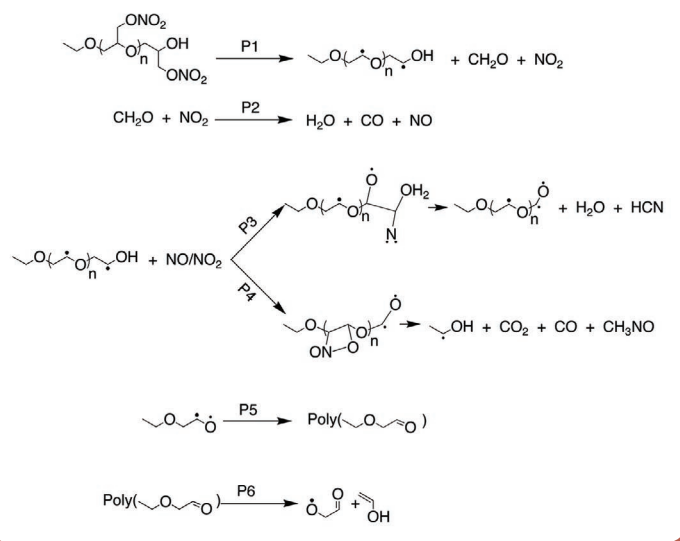
Figure 3. *Reaction mechanism controlling the thermal decomposition of PGN prepolymer. Pathways P1 and P2 are the direct reactions of the CH_2-O-NO_2 functional moiety. Pathways P3 and P4 are the interaction of the gas products with the reactive backbone. P5 and P6 are the formation and subsequent decomposition of a non-volatile residue.*

for the combustion reactions of the cured PGN rubber. Any substantial alteration of the decomposition process could affect either the combustion mechanism, through a change in the distribution of the evolved products, or the combustion kinetics, through a change in the evolution rates of the gaseous products. The reaction mechanism developed from this investigation indicates that the decomposition process is not affected by the OH end-modification. Based on these results, it would not be expected that the OH end-modification would affect the combustion kinetics of the resulting, cured PGN rubber.